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***Ab initio* study of oxygen adsorption on the Ti(0001) surface**

Shi-Yu Liu¹, Fu-He Wang^{1,3}, Yun-Song Zhou¹ and Jia-Xiang Shang²

¹ Department of Physics, Capital Normal University, Beijing 100037, People's Republic of China

² School of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing 100083, People's Republic of China

E-mail: wfh-phy@mail.cnu.edu.cn

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Abstract

The adsorption of oxygen atoms on the Ti(0001) surface is investigated by the use of *ab initio* total-energy density-functional methods within the generalized gradient approximation. Two kinds of supercell model (a single-layer and a multiple-layer adsorption model) are designed to study the preference of occupation sites for oxygen atoms. In the single-layer adsorption model, the oxygen atoms are restricted in the same adsorption layer. In the multiple-layer adsorption model, the adsorbed oxygen atoms occupy sites in different adsorption layers at the same time. Our calculated results show that the surface face-centred cubic (SFCC) sites are the most favourable sites for oxygen atoms to occupy when the oxygen coverage is 0.25 monolayer (ML); however, the system with one oxygen atom occupying the SFCC sites and the other one occupying the octahedral sites between second and third Ti layers (Octa(2, 3)) is the most stable configuration when the oxygen coverage is 0.50 ML. As the oxygen coverage is increased to 1.0 ML, each of the oxygen atoms prefers occupying the SFCC and octahedral sites such as Octa(2, 3), Octa(4, 5) and Octa(6, 7) in the alternate layers, respectively. It can be found that there are strong repulsive interactions between the adsorbed oxygen atoms when they occupy adjacent interstitial sites. Our calculated results of the work functions and the total density of states with the multiple-layer adsorption model are in good agreement with experimental results of work function change and ultraviolet photoelectron spectroscopy. It should be noticed that the multiple-layer adsorption model must be taken into account for oxygen adsorption on the Ti(0001) surface.

³ Author to whom any correspondence should be addressed.

1. Introduction

Titanium is utilized in many applications such as space shuttles, aircraft, automobiles, medicine and computers, because of its superior properties of light weight, strength, anticorrosive nature and heat resistance [1]. However, Ti surfaces are so reactive as to easily form compounds with any molecule except for rare gases. Passivation of the Ti surface with oxides and nitrides or modification of it with ion implantation is therefore of practical importance. Oxidation of metal surfaces is a complex process, which includes the dissociative chemisorption of oxygen on a clean surface, the diffusion of oxygen atoms, and the formation of a film of metal oxide.

It is generally believed that dissociative adsorption of light element gases such as hydrogen, nitrogen, and oxygen takes place on metal surfaces, and adatoms are chemisorbed on sites above the metal surface, such as oxygen atoms chemisorbed on the common metal Al(111) [2], transition metal Ru(0001) [3], Rh(111) [4], Pd(111) [5], Ag(111) [6], and so on. This is due to the binding of the adatom onto the surface being usually more stable than that in the subsurface or bulk site. There are, however, exceptions. The recent result of first-principles calculation for the O/Mg(0001) system shows that tetrahedral subsurface sites between the first and second metal layers are the most favourable for oxygen adsorption. Thus the oxidation of the common metal Mg is a subsurface process [7]. For most subsurface chemisorption systems, adsorption sites are found to be (or assumed to be) between the first and second layer of the host, for example in the O/Mg(0001) system [7]. Rather interestingly, Yamamoto *et al* [8] performed first-principles total energy calculations within the local density approximation (LDA) for the adsorption of oxygen on the Zr(0001) surface. They found that oxygen atoms favour the adsorption sites between the second and the third layer in the O/Zr(0001) system. Recently, Jomard *et al* [9] presented a detailed investigation of the adsorption of oxygen atoms on the Zr(0001) surface based on *ab initio* total-energy calculations within both the LDA and the generalized gradient approximation (GGA). They pointed out that the LDA and GGA lead to a different relative stability of these different sites. Their LDA-based calculations show that the most energetically favourable sites are the octahedral ones located between the second and the third zirconium layers, in agreement with the result of Yamamoto *et al* [8], while the GGA-based results show that the most favourable sites are the surface face-centred cubic (SFCC) sites. So it is very interesting for us to investigate the oxidation of Ti, which is in the same group, by the use of *ab initio* total-energy density-functional methods within the GGA.

The titanium(0001)–oxygen system has been extensively studied by experimental investigations. For the single-crystal Ti(0001) surface, detailed studies of the initial oxidation kinetics were performed with respect to a $p(2 \times 2)$ oxygen adsorption structure at low oxygen coverage by low-energy electron diffraction (LEED) [10], of the lattice site of adsorbed oxygen by x-ray photoelectron diffraction [11], of the oxygen adsorption state by photon-stimulated desorption [12], and of the electronic structure by electron energy-loss spectroscopy (EELS) [13] and ultraviolet photoelectron spectroscopy (UPS) [12, 13]. A work function of 4.6 ± 0.2 eV was measured for the clean Ti(0001) surface by experiment [12]. It was also observed that the work function decreased at the beginning of the oxygen adsorption on the Ti(0001) surface, then increased when the O₂ dose was increased, and that a subsequent plateau was reached when the O₂ dose was high enough [12]. An initially diffuse $p(2 \times 2)$ LEED pattern formed at room temperature was significantly improved upon a 250 °C flash anneal. This was accompanied by an abrupt decrease of 0.15 eV in the work function, although Auger electron spectroscopy (AES) revealed no decrease in the amount of oxygen on the surface [10]. The UPS curve showed only one peak on the clean Ti(0001) surface. Upon exposure to oxygen, a new peak in the UPS spectrum appeared at 5.9 eV as a shoulder on the high binding energy

side of the initial peak. With increasing exposure to oxygen, the new peak was broadened and the centre of the new peak also shifted to higher binding energy [12]. Although most of the previous studies were performed at room temperature, further interesting results were reported for oxidation at high temperature. Vaquila *et al* [14] reported that no oxygen is detected on the surface of titanium when temperature was over 400 °C, indicating the existence of a metallic Ti layer on the outermost surface during oxidation. Thus the diffusion of oxygen into bulk Ti is considerably enhanced on elevating the temperature above 400 °C. Recently, high-resolution photoelectron spectroscopy using synchrotron radiation was applied for monitoring in real time the chemically shifted components of O 1s and Ti 2p core levels during initial oxidation on the Ti(0001) surface at 405 °C. It was also found that there still remains metallic Ti on the surface after the formation of oxide at 405 °C [15].

How can we understand the above experimental results? What is the physical reason behind the experimental phenomena? To answer these questions, we use an *ab initio* approach based on the density-functional theory (DFT) to study the adsorption of oxygen atoms on the Ti(0001) surface. The remainder of this paper is organized as follows. In section 2, we give details of the first-principles total energy calculations. The results for O adsorbed on the Ti(0001) surface as a function of the oxygen coverage are presented in section 3, where the energetics, the favourite oxygen occupation sites and the electronic properties are also analysed and compared with experimental results. Finally, in section 4, our results are summarized.

2. Computational details and models

We performed DFT calculations [16, 17] within the generalized-gradient approximation (GGA) of the PW91 [18] form for electron exchange and correlation, using the Vienna *ab initio* simulation package (VASP) [19–21]. Here we employed the projector-augmented wave (PAW) method [22], as implemented by Kresse and Joubert [23]. The PAW method is an all-electron DFT technique (within the frozen-core approximation) with the computational efficiency of pseudopotential techniques. We tested k -point sampling and kinetic energy cutoff convergence for all supercells. As a result of the convergence tests, we use a kinetic energy cutoff of 400 eV for all calculations. For bulk Ti, a $15 \times 15 \times 15$ Monkhorst–Pack k -point mesh [24] for the primitive cell is used. The calculated lattice constants are $a = 2.920 \text{ \AA}$ and $c = 4.618 \text{ \AA}$, which agree very well with experiment [25] and previous DFT-GGA results [26].

The structure model of the oxygen-adsorbed Ti(0001) system is shown in figure 1. For the study of O/Ti(0001) systems, we use supercells containing a nine-layer metal slab and a vacuum gap equivalent to seven bulk-metal layers. Oxygen is placed on one side of the slab where the induced dipole moment is taken into account by applying a dipole correction [27, 28]. We have checked the convergence with respect to the slab size. The difference of the binding energy of oxygen atom on Ti(0001) surfaces with seven-layer and nine-layer metal slabs is less than 0.01 eV. In figure 1, the various oxygen adsorption sites considered in our calculations are shown schematically for a range of oxygen coverage. We will use the symbol Octa(i, j) to denote oxygen atoms at the octahedral sites between the i th and the j th metal layer; whereas Tetra($i, j: ak$ (or bk)) means the oxygen atoms at the tetrahedral sites located directly above (or below) the k th metal layer and between the i th and the j th metal layers. A $p(2 \times 2)$ surface cell was used with 9×9 Monkhorst–Pack k -points in the surface Brillouin zone. There are four Ti atoms in each layer in the surface cell. Here, the definition of one monolayer (1 ML) for the coverage of oxygen is that there are four oxygen adatoms in the surface cell. In our calculations, the bottom three titanium layers were fixed at their bulk truncated structure; the other atoms were relaxed until the forces on each of them were less than 0.01 eV \AA^{-1} .

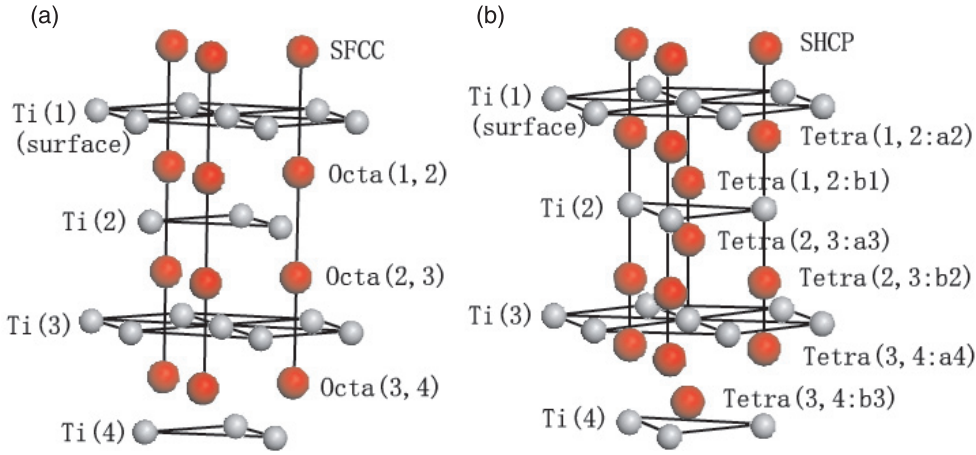


Figure 1. The structure model of the possible adsorption sites for oxygen atoms to take at the Ti(0001) surface. Small grey circles represent Ti atoms and large black circles represent the possible adsorption sites for oxygen atoms. In (a) and (b), the octahedral and tetrahedral sites are shown respectively. Here Octa(i, j) in (a) means the octahedral site between the i th and the j th metal layer. Tetra($i, j: ak$ (or bk)) in (b) means the tetrahedral site located above (or below) the k th metal layer and between the i th and the j th metal layers.

(This figure is in colour only in the electronic version)

We have designed two kinds of model: the single-layer and multiple-layer adsorption models. In the single-layer adsorption model, oxygen atoms are restricted to the same adsorption layer. In the multiple-layer adsorption model, the oxygen atoms can be distributed into different adsorption layers at the same time.

3. Results and discussion

3.1. The relative stability of oxygen adsorption sites

The stability of various O/Ti(0001) systems is analysed by calculations of the average binding energy. The average binding energy per oxygen atom as a function of the coverage Θ is

$$E_b(\Theta) = \frac{1}{N_{\text{O}}^{\text{atom}}} [E_{\text{O/Ti(0001)}}^{\text{slab}}(\Theta) - (E_{\text{Ti(0001)}}^{\text{slab}} + N_{\text{O}}^{\text{atom}} E_{\text{O}}^{\text{atom}})], \quad (1)$$

where $N_{\text{O}}^{\text{atom}}$ is the number of oxygen atoms in the unit cell, and $E_{\text{O/Ti(0001)}}^{\text{slab}}$, $E_{\text{Ti(0001)}}^{\text{slab}}$ and $E_{\text{O}}^{\text{atom}}$ represent the total energies per unit cell of the oxygen-adsorbed Ti slab, the clean Ti slab, and a free oxygen atom, respectively. The total energy of the free oxygen atom is calculated in a cubic cell with a side length of 10 Å with $4 \times 4 \times 4$ Monkhorst-Pack k -point sampling. The calculated total energy of a free oxygen atom is -1.63 eV.

3.1.1. Calculations with the single-oxygen-layer adsorption model. In the single-layer adsorption model, the oxygen atoms are restricted to the same layer. The results of our calculated binding energies are listed in table 1. The SFCC sites are slightly more favourable than the surface hexagonal close-packed (SHCP) sites by about 0.2 eV for all coverages. If the oxygen atoms penetrate the Ti top layer, the most probable sites for oxygen atoms to occupy are the octahedral and the tetrahedral interstitial sites in the Ti host. From table 1, we can see that the subsurface tetrahedral sites are always less stable compared with the octahedral sites.

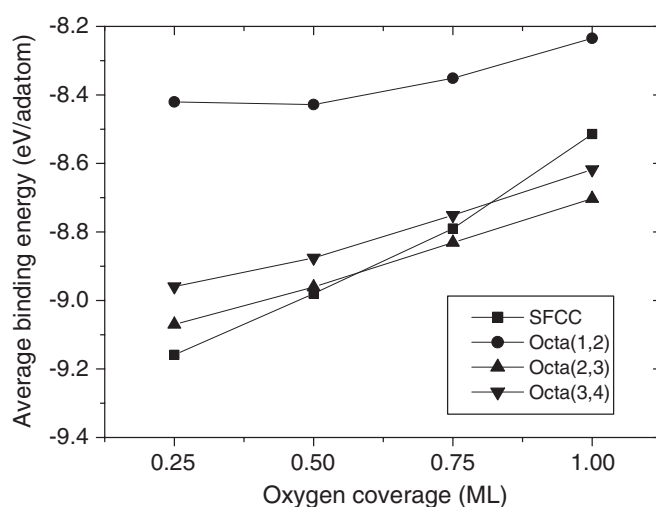


Figure 2. The calculated binding energies for oxygen atoms to occupy different adsorption sites in the single-layer adsorption model at different oxygen coverage.

Table 1. The average binding energy E_b (eV) per oxygen atom when oxygen atoms occupy different adsorption sites with the single-layer adsorption model for the oxygen coverage $0.25 \leq \Theta \leq 1.00$ ML.

Adsorption site	0.25 ML	0.50 ML	0.75 ML	1.00 ML
SFCC	-9.16	-8.98	-8.79	-8.51
Octa(1, 2)	-8.42	-8.43	-8.35	-8.23
Octa(2, 3)	-9.07	-8.96	-8.83	-8.70
Octa(3, 4)	-8.96	-8.88	-8.75	-8.62
SHCP	-8.90	-8.73	-8.57	-8.39
Tetra(1, 2: a2)	Unstable			-7.64
Tetra(1, 2: b1)	-7.18			-7.85
Tetra(2, 3: a3)	-6.97			-7.91
Tetra(2, 3: b2)	-7.33			-7.88
Tetra(3, 4: a4)	-7.35			-7.88
Tetra(3, 4: b3)	-7.22			-7.93

From figure 1, we can easily see that the SFCC sites can be regarded as the continuation of the subsurface octahedral sites, while the SHCP sites are directly above the tetrahedral sites. In the subsurface configurations, the interstitial vacancy of the tetrahedral sites has a much smaller geometrical volume compared with that of the octahedral sites. This will lead to large strain and mandate a large relaxation of the host lattice when oxygen atoms take the tetrahedral sites. This probably contributes to the higher energy for oxygen atoms to occupy the tetrahedral sites.

For further inspection, we plot the average binding energies of oxygen atoms when they occupy the SFCC or octahedral interstitial sites in figure 2. It can be found that for the coverage of 0.25 and 0.50 ML the most energetically favourable sites are the SFCC sites. In this case, our calculations show that the binding energy for the oxygen atoms occupying the SFCC sites is lower than that for them occupying Octa(1, 2) sites, by about 0.54 eV. It is thus rather unlikely that the Octa(1, 2) sites can compete with the SFCC sites. While the Octa(2, 3) sites are the second most stable sites for oxygen atoms to occupy, the binding energy of oxygen atoms is

Table 2. The average binding energy E_b (eV) per O atom when oxygen atoms occupy different adsorption sites with the multiple-layer adsorption model for the oxygen coverage $0.50 \leq \Theta \leq 2.00$ ML.

Adsorption site	0.50 ML	1.00 ML	2.00 ML
SFCC + Octa(1, 2)	−8.88	−8.82	−8.37
Octa(1, 2) + Octa(2, 3)	−8.76	−8.67	−8.25
SFCC + Octa(2, 3)	−9.14	−9.02	−8.67
Octa(2, 3) + Octa(3, 4)	−8.97	−8.88	−8.52
Octa(2, 3) + Octa(4, 5)	−9.06	−8.99	−8.78
SFCC + Octa(2, 3) + Octa(4, 5) + Octa(6, 7)		−9.10	−9.02

only 0.09 eV for $\Theta = 0.25$ ML and 0.02 eV for $\Theta = 0.50$ ML higher than that of them when they occupy the SFCC sites. Turning to higher coverage of 0.75 and 1.00 ML, the octahedral sites Octa(2, 3) become the most stable sites. In this case, our calculations show that the binding energy of oxygen atoms at the Octa(2, 3) sites is lower than that at the Octa(1, 2) sites by about 0.47 eV. It is thus rather unlikely that the Octa(1, 2) sites can compete with the Octa(2, 3) sites. The binding energy of oxygen atoms at the SFCC sites is 0.04 eV for 0.75 ML and 0.19 eV for 1.00 ML higher than that of them at Octa(2, 3) sites. Our results support the subsurface adsorption model for oxygen coverage of 0.75 and 1.00 ML in the single-layer adsorption model. However, the most favourable sites are found to be those between the second and third layers, rather than those between the top and second layers. This indicates that the oxygen atoms prefer occupying the sites between the second and third layers at higher oxygen coverage.

From figure 2, another feature can be found: it is that the average binding energy per oxygen atom is increased when the coverage of oxygen is increased. Such a behaviour reflects the repulsive adsorbate–adsorbate interactions with the decrease of O–O distance.

3.1.2. Calculations with the multiple-layer adsorption model. From the calculated results with the single-layer adsorption model, it was found that there are repulsive interactions between two adsorbed oxygen atoms when they occupy the sites that are closest together. What would be the result when the oxygen atoms occupy sites with longer distances between them for the same coverage? In order to answer this question, we have designed a multiple-layer adsorption model. In this model, the oxygen atoms can be distributed into different layers at the same time. The calculated binding energies are presented in table 2. For an oxygen coverage of 0.50 ML, the average binding energies of oxygen atoms in the systems with oxygen atoms occupying the combination sites such as SFCC and Octa(1, 2), Octa(1, 2) and Octa(2, 3), Octa(2, 3) and Octa(3, 4), etc in adjacent layers are higher than in systems with oxygen atoms occupying the combination sites such as SFCC and Octa(2, 3), Octa(2, 3) and Octa(4, 5), etc in alternate layers. In this case, the system is the most stable when one oxygen atom occupies the SFCC site and the other one occupies the Octa(2, 3) site.

For the oxygen coverage of 1.00 ML, as discussed for the oxygen coverage of 0.50 ML, each of the four oxygen atoms prefers occupying the SFCC and octahedral sites in each alternate layer, respectively. This is the most stable system, with each of the four oxygen atoms occupying SFCC, Octa(2, 3), Octa(4, 5) and Octa(6, 7), respectively. However, it should be noticed that the average binding energy of oxygen atoms in the system with two oxygen atoms occupying SFCC sites and the other two occupy Octa(2, 3) sites is only 0.08 eV higher than that of them in the most stable system. So this system can compete with the most stable system, especially at the initial stage of oxidation of the Ti(0001) surface.

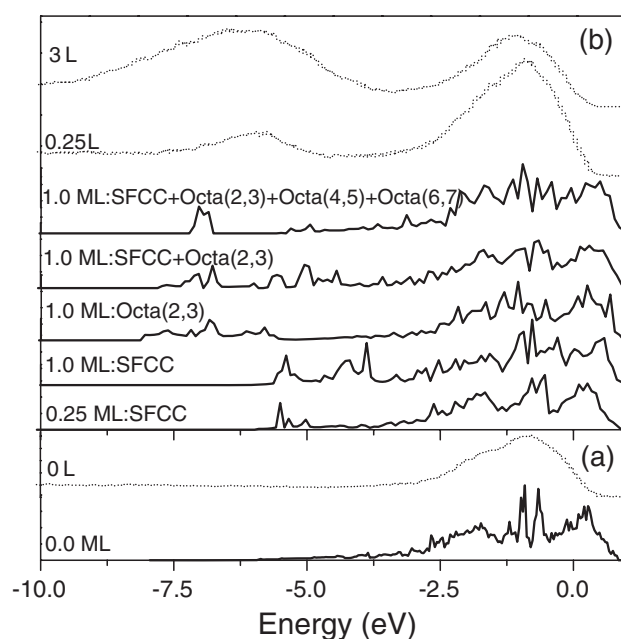


Figure 3. The comparison of the total density of states for selected O/Ti(0001) systems with the experimental UPS. The dotted lines are the UPS spectrum quoted from [12]. The oxygen exposures are 0.0, 0.25 and 3.0 L.

For the oxygen coverage of 2.00 ML, we can infer from the above discussion about $\Theta = 1.0$ ML that the system with each of the eight oxygen atoms occupying the SFCC and octahedral sites in each alternate layer, such as Octa(2, 3), Octa(4, 5), Octa(6, 7), Octa(8, 9), Octa(10, 11), Octa(12, 13) and Octa(14, 15), is the most stable. There are so many systems for higher oxygen coverage that we cannot calculate each of them. It is unnecessary for us to calculate all of them, if we only interested in the initial stage of the oxidation of titanium. As discussed for the oxygen coverage of 1.00 ML, in this case, the average binding energy of oxygen atoms in the system with each pair of the eight oxygen atoms occupying the SFCC and octahedral sites in each alternate layer, such as Octa(2, 3), Octa(4, 5) and Octa(6, 7), should be almost the same as that of them in the most stable system with each of the eight oxygen atoms occupying the SFCC and octahedral sites in each alternate layer, respectively. These two systems can compete with each other. The above results show that there are strong repulsive interactions between the adsorbed oxygen atoms if they occupy adjacent interstitial sites.

3.2. Comparison with experimental results

3.2.1. Comparison of total density of states with UPS. In order to examine the efficiency of our adsorption models, we have calculated the total density of states (TDOS) for clean and oxygen-adsorbed Ti(0001) surfaces with both the single-layer and the multiple-layer adsorption models. The selected calculated results are compared with the UPS experimental results, which are quoted from [12], in figure 3. The TDOS of the clean Ti(0001) surface mainly distributes in the energy range from -3.0 to 0.9 eV (see figure 3(a)). In this case, the calculated result is in good agreement with the experimental result. Upon oxygen adsorption, the most stable adsorption sites for oxygen atoms are SFCC sites when the oxygen coverage is 0.25 ML. In this

case, a new state in the energy close to -5.5 eV is observed when the TDOS of the O-adsorbed surface is compared with that of the clean surface (see figure 3(b)). This is in good agreement with the experimental result that a new peak appeared at the electron binding energy of 5.9 eV in the UPS spectrum when the oxygen exposure is 0.25 langmuirs (L) [12]. The electronic states in the energy range around -5.5 eV are mostly composed of the oxygen 2p states and the Ti 3d and 4s states.

When the coverage of oxygen is increased to $\Theta = 1.00$ ML, there are four oxygen atoms in the unit cell. In this case, the TDOS of several possible adsorbed systems with both the single-oxygen-layer and the multiple-layer adsorption models are calculated, and only three of them are selected to be presented in figure 3. At this coverage, when all the four oxygen atoms only occupy the SFCC sites, the distribution of the TDOS is similar to that of the system when 0.25 ML of oxygen adsorbed on SFCC sites. The new peaks are mainly located from -3.7 to -5.6 eV when the TDOS is compared with that of the clean surface. When all the four oxygen atoms only occupy the Octa(2, 3) sites, new peaks only appear in the energy range from -5.7 to -8.0 eV in the TDOS. However, there are no peaks in the energy range from -3.7 to -5.6 eV. When two oxygen atoms occupy the SFCC sites and the other two occupy Octa(2, 3) sites at the same time, the main new peaks appear in the wide range of -4.4 to -7.6 eV. When each of the four oxygen atoms occupies the SFCC, Octa(2, 3), Octa(4, 5) and Octa(6, 7) sites, at the same time in the most stable system, the main new peaks appear in the wide range of -4.8 to -7.2 eV. The UPS experimental results [12] show that the new peak was broadened and the centre of the new peak also shifted to the high electron binding energy (corresponding to the lower energy of electrons in our theoretical results), when the oxygen exposure is higher (for example 3.0 L). Comparing all the theoretical results with experiment, the single-layer adsorption model is excluded when the coverage of oxygen is higher than 0.5 ML. Only the TDOSs with the multiple-layer adsorption models are in good agreement with experimental results. However, it is hard to exclude either from both the system with oxygen atoms occupying the combination of SFCC and Octa(2, 3) sites and the combination of SFCC, Octa(2, 3), Octa(4, 5) and Octa(6, 7) sites.

3.2.2. Changes in the work function. Our calculated work function for the clean surface is 4.45 eV, which agrees very well with experimental values of 4.6 ± 0.2 eV [12] and 4.45 eV [25] and the previous DFT-GGA result, 4.42 eV [26]. In comparison to the clean Ti(0001) surface, the changes in work functions $\Delta\phi$ for the different adsorbed systems are shown in figure 4 for the range of oxygen coverage $0 \leq \Theta \leq 1$ ML with both the single-layer and multiple-layer adsorption models.

It was found by experiments [12] that the work function decreased at the beginning of the oxygen adsorption on the Ti(0001) surface, then increased when the O_2 dose was increased, and a subsequent plateau was reached when the O_2 dose was high enough. It is clearly seen that, in the single-layer adsorption model (see figure 4(a)), the changes in the work functions of the most stable systems cannot accord with the experiment results. Now, we discuss the changes with respect to the multiple-layer adsorption model. The changes of the work functions of the most stable systems for the oxygen coverage from 0.00 to 1.00 ML are plotted in figure 4(b). When the oxygen coverage Θ is 0.25 ML, the work function is decreased by 0.24 eV, then it is increased as the coverage Θ increases. As discussed in section 3.2.1, oxygen atoms not only occupy the SFCC sites, but also penetrate into the subsurface to occupy the Octa(2, 3), etc sites, when the coverage Θ is higher than 0.50 ML. From the point of view of energy, the average binding energy of oxygen atoms in the system with oxygen atoms only occupying SFCC sites is about 0.5 eV higher than that in the system with two oxygen atoms occupying SFCC sites

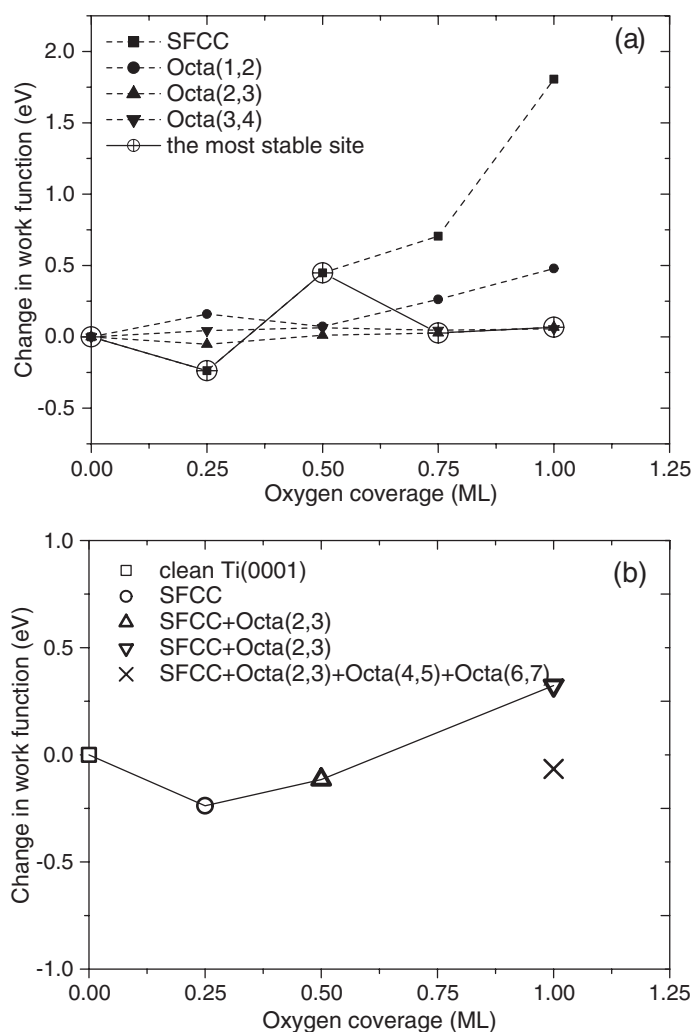


Figure 4. The calculated changes in work functions of the systems with oxygen atoms occupying different sites as a function of oxygen coverage. (a) The changes in work functions of the systems with the single-layer adsorption model. As a guideline, the trend of work functions of the most stable systems is plotted by a solid line. (b) The trend of work functions of the most stable systems in both the single-layer and multiple-layer adsorption models.

and the other two occupying the Octa(2, 3) sites, when Θ is 1.00 ML. It is hard for the system with oxygen atoms only occupying SFCC sites to compete with the system with oxygen atoms occupying both the SFCC and Octa(2, 3) sites. However, the second system with oxygen atoms occupying both the SFCC and Octa(2, 3) sites can compete with the most stable system with each of the four oxygen atoms occupying the SFCC, Octa(2, 3), Octa(4, 5) and Octa(6, 7) sites, because the difference of the average binding energy of oxygen atom is very small (0.08 eV). At the initial stage of oxidation, the probability of the occurrence of the system with oxygen atoms occupying both the SFCC and Octa(2, 3) sites may be larger than that of the most stable system, because the oxygen atoms must penetrate into deeper sites in the most stable system.

Taking the above discussion into account, the trend of the changes in the work function of the almost most stable systems predicted by the multiple-layer adsorption model agrees well with the work function experiments [12].

Another point revealed by experiments [10] should be noticed: a very diffuse $p(2 \times 2)$ LEED pattern was formed at room temperature when the clean surface was exposed to oxygen, and the pattern was significantly improved when the sample was flashed to 250 °C; at the same time, the work function of the sample was abruptly decreased by 0.15 eV, and no decrease in the amount of oxygen on the surface was revealed by AES; with additional exposure to oxygen, the work function continued its cycle of increasing with exposure and abruptly decreasing upon a flash anneal. Based on the above experimental results, the authors proposed that there are two chemisorption states, α and β , for the adsorbed oxygen atoms on Ti(0001) surface. In the α state, a well-ordered $p(2 \times 2)$ LEED pattern was formed, and the work function of the system was lower than that of the clean surface. In the β state, a disordered structure was formed, and the work function of the system was higher than that of the clean surface. Heating converted the β state to the α state. Now, we discuss our theoretical results. It can be seen from figure 4 that the work function of the most stable system with oxygen occupying the SFCC sites is 0.24 eV below that of the clean surface when Θ is 0.25 ML. In this case, the surface structure is just $p(2 \times 2)$. When Θ is 0.50 ML, oxygen atoms may occupy the SFCC sites first, and the work function is 0.45 eV higher than that of the clean surface; then oxygen atoms will occupy both the SFCC and Octa(2, 3) sites and the system will change into the most stable state after the system is flashed to 250 °C. In this case, the work function of the system is 0.11 eV lower than that of the clean surface, and the surface structure is changed into $p(2 \times 2)$ again. Of course, the amount of oxygen at the surface is not changed when it is detected by AES. When Θ is 1.00 ML, two oxygen atoms may occupy the SFCC sites and the other two occupy the Octa(2, 3) sites first, and the work function is 0.32 eV higher than that of the clean surface; then each of the four oxygen atoms will occupy the SFCC, Octa(2, 3), Octa(4, 5) and Octa(6, 7) sites and the system will change into the most stable state after the system is flashed to 250 °C again. In this case, the work function of the system is 0.07 eV lower than that of the clean surface, and the surface structure is changed into $p(2 \times 2)$ again. When we compare our theoretical results with the experimental results, we can find that the α states in the experiments [10] are the states in our most stable systems, and the β states in the experiments are the states in our metastable systems, in which more oxygen atoms are adsorbed on the surface layers.

It is generally believed that the work functions increase (decrease) when negatively charged adatom such as oxygen adsorb above (below) the surface [29]. Intuitively, we expect that the charge is transferred from the Ti atoms to the more electronegative oxygen atoms, and if the oxygen atoms are above the surface, the surface dipole will tend to increase the work function, whereas if the oxygen atoms are just below the surface, the dipole points in the opposite direction and decreases the work function. The change in $\Delta\phi$ should decrease as the oxygen atoms are buried deeper into the bulk and are screened by the Ti conduction electrons. Our calculated results support this assumption when the coverage of oxygen is higher than 0.25 ML. However, we find an unusual phenomenon that the work function of the system with the coverage of 0.25 ML of oxygen occupying the surface overlayer SFCC sites decreases in comparison to the clean surface. Similar behavior has also been found for the O/Al(111) system by theory [2]. The unusual behaviour was interpreted by Leung *et al* based on density-functional theory [30]. They pointed out that work function changes are not only decided by the quantity and the sign of the charge transferred, but also by the details of the charge redistribution, leading in some cases to a strong dependence of the work function change on the orientation of the substrate.

4. Conclusion

The structural and electronic properties of oxygen atoms adsorbed at the Ti(0001) surface have been investigated by the use of *ab initio* total-energy density-functional methods within the generalized-gradient approximation and supercell approach. Two kinds of model were used. One was the single-layer adsorption model, in which the adsorbed oxygen atoms occupied sites in the same adsorption layer. The other one was the multiple-layer adsorption model, in which the adsorbed oxygen atoms occupied sites in different adsorption layers. In the single-layer adsorption model, the most stable sites for oxygen atoms are the SFCC sites when the oxygen coverage is less than 0.50 ML, whereas the energetically most favourable sites for oxygen become the octahedral sites Octa(2, 3) between the second and third layers, when the coverage is 0.75 and 1.00 ML. The calculated results with the multiple-layer adsorption model have shown that the combination of SFCC and Octa(2, 3) is the most stable combination of sites for oxygen to occupy when the oxygen coverage is 0.50 ML. When the oxygen coverage $\Theta \geq 1.00$ ML, each of the oxygen atoms prefers occupying the SFCC and octahedral sites such as Octa(2, 3), Octa(4, 5), etc in alternate layers, respectively. It can be concluded that there are repulsive interactions between the adsorbed oxygen atoms when they occupy adjacent interstitial sites. Our calculated results of the work functions and the TDOS with the multiple-layer adsorption model are in good agreement with experimental results of work function change [10, 12] and UPS [12]. The changes in the work functions and the adsorption states α and β of oxygen proposed from the experiments [10] can be well explained by our theoretical results. It could be concluded that the multiple-layer adsorption model must be taken into account for oxygen adsorption at the Ti(0001) surface.

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